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(71) Applicant(s)

**Röhm GmbH**

**(Incorporated in the Federal Republic of Germany)**

**Postfach 4242, Kirschenallee, D-64293 Darmstadt,  
Federal Republic of Germany**

(72) Inventor(s)

**Günther Ittmann**

**Manfred Krieg**

(74) Agent and/or Address for Service

**Frank B Dehn & Co**

**Imperial House, 15-19 Kingsway, LONDON,  
WC2B 6UZ, United Kingdom**

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**None**

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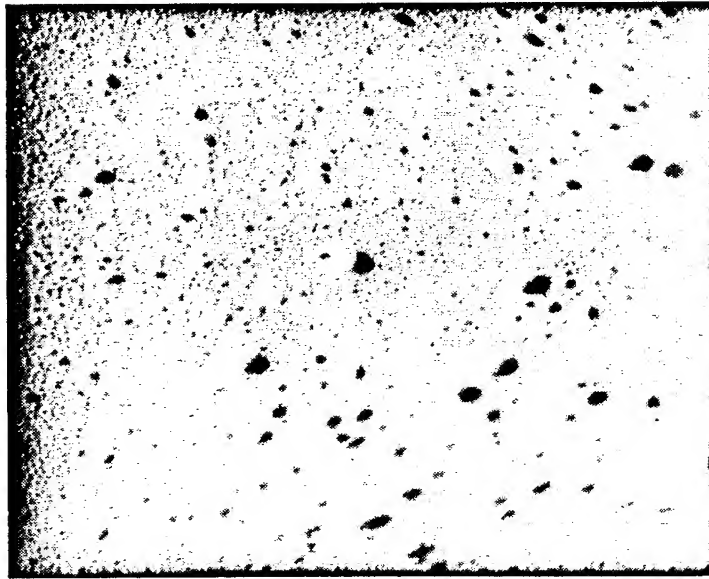
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(54) **Expanded polymer materials**

(57) The invention relates to a process for preparing filled, expanded polymer materials based on polymethacrylate. An initial solution VL consisting of 5 to 70 parts by weight of methylmethacrylate and 1 to 15 parts by weight of polymethylmethacrylate prepolymer PP is prepared into which a particle-like inorganic filler FS in amounts of 30 to 80 wt.% based on the resultant suspension is introduced, while stirring rapidly, thereby forming a suspension. Gaseous or solid carbonic acid, in fine distribution, is uniformly introduced into the initial solution or suspension, whereupon, as a result of external heating or the heat effect of the polymerisation process, preferably initiated by the Redox initiator, the carbon dioxide is expelled while the polymerisation takes place. At the end of the polymerisation, removal from the mould can be effected.

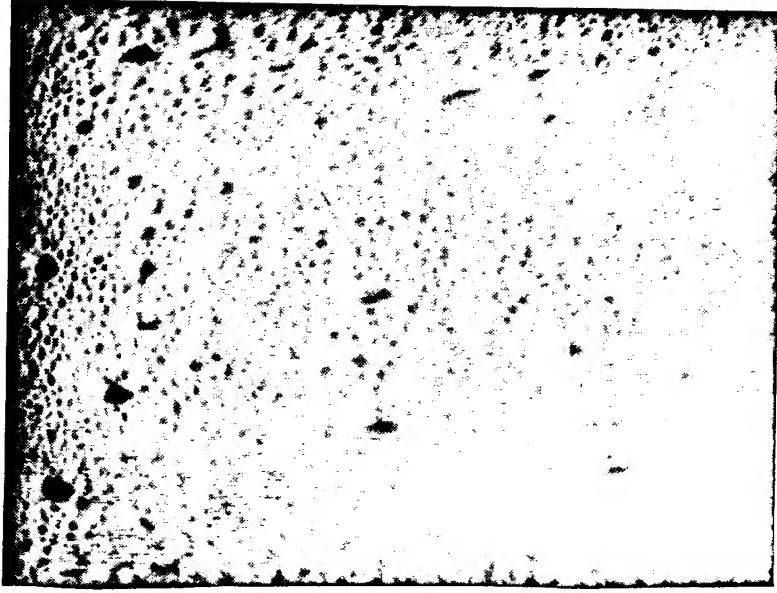
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FIG.1.



5% CO<sub>2</sub>-SNOW

FIG.2.



10% CO<sub>2</sub>-SNOW

1/2

FIG.3.



5% CO<sub>2</sub>-ICE (GROUND)

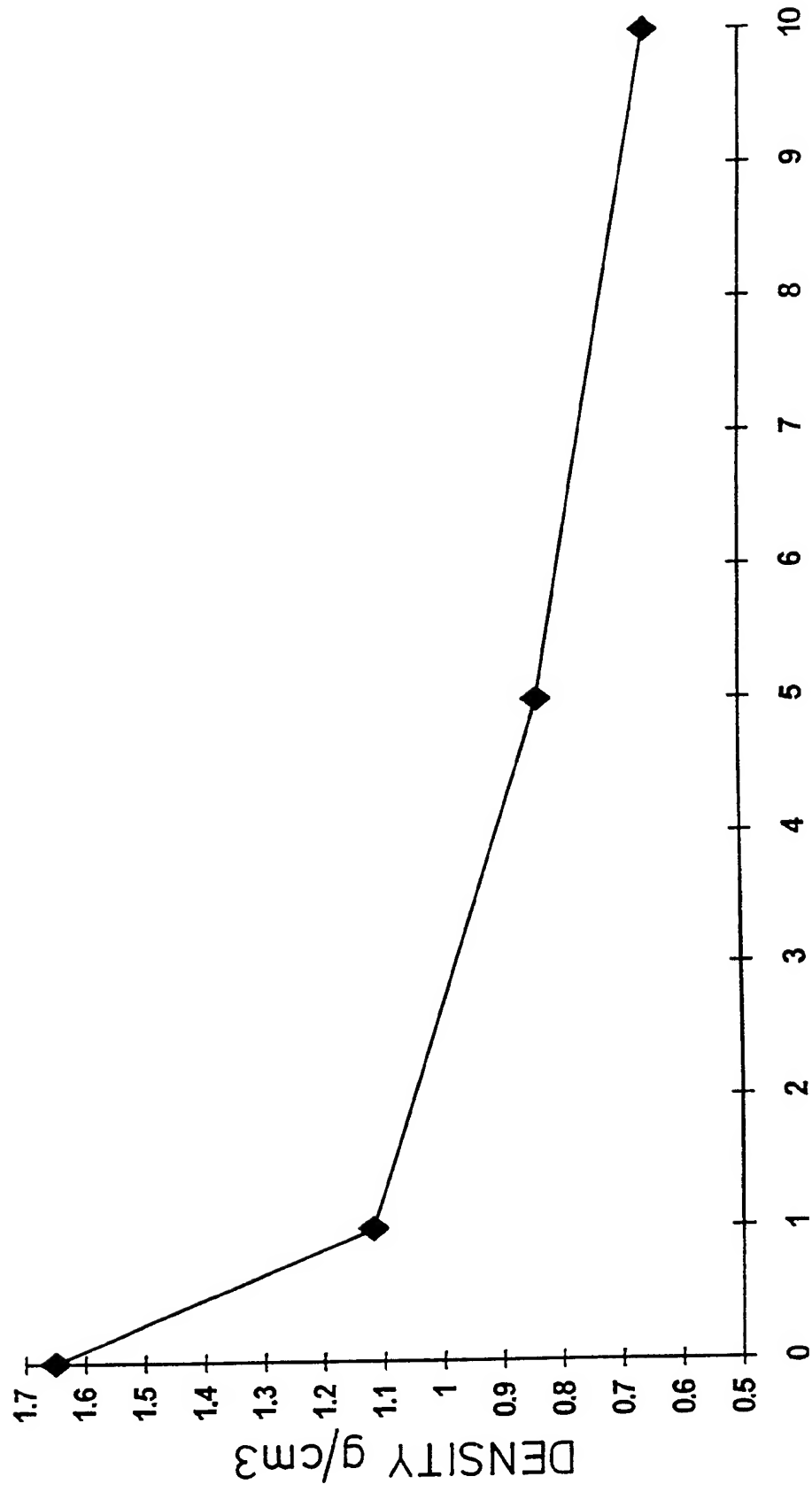


FIG.4.

"Expanded Polymer Materials"

5           The invention relates to highly filled, expanded polymer materials based on polymethacrylate.

          Highly filled cast resins, for example based on polymethylmethacrylate (PMMA) have for a long time enjoyed commercial success (Cf. EP 218 866; US-PS 3 847  
10 865; US-PS 4 221 697, US-PS 4 251 576, US-PS 4 826 901; US-PS 4 786 660). Such polymer materials enriched with mineral fillers, which may, for example, be used for kitchen sinks, in the sanitary field and generally as plate materials in the building industry are normally  
15 well able, particularly in modern designs, to meet industrial requirements with regard to appearance, durability, and workability. They are, however, comparatively heavy materials. PMMA with a filler content of 60 to 70 wt.% of silicon dioxide or aluminium  
20 hydroxide has, for example, a density of 1.8 g/cm<sup>3</sup>. Experiments to produce expanded polymer material have been conducted over a long period.

          DE-P 10 17 784 discloses a process for preparing porous moulded bodies, mainly made of PMMA, in which  
25 carbon dioxide snow is added to the polymer/monomer mixture in order to obtain at least partially the necessary low temperature and simultaneously a porous structure of the product formed during polymerisation. The same patent discloses that dyes, pigments and/or  
30 fillers may be added to the polymerisable compound. According to FR-PS 1 055 058 one method normally used for preparing porous moulded bodies is the heating of thermoplastic plastics containing gases in solution above their softening point, whereby the plastics matrix  
35 is expanded by the expanding gases. Other patents disclose expanded polymer material, in which a propellant is produced by a water-containing polymer

component acting on a calcium carbide-containing polymer component (South African Patent 68.08312), or polymer materials expanded by means of peroxide compounds (Japan-Kokai 78,105 565; Chem. Abstr. 90,39 662a; Japan  
5 Kokai 75,151 278, Chem. Abstr. 84,151 530h).

In order to prepare cast resins, the emulsification of up to 50 wt.% of the water in a filled suspension of methylmethacrylate is known from EP 0 503 156. After  
10 hardening, the water is expelled from the shaped cast by heating. A foam-like, highly filled material remains.

Technology has to meet different quality requirements when preparing highly filled expanded polymethylmethacrylate, i.e. a material containing from at least 40 up to 80 wt.% of an inorganic filler as  
15 opposed to the preparation of "porous, moulded bodies mainly consisting of methylpolymethacrylates" according to DE-PS 10 17 784. The method used here is a variant of the chamber-polymerisation process in which carbon dioxide snow in a homogenous distribution is, if  
20 possible, added to a conventional initiator-containing prepolymer whilst stirring, and this mixture is filled into the moulding chamber. This mixture may be cast below 0°C and upon heating it gels to form a solid compound. Thus, the prior art does not provide a direct  
25 method for the preparation of expanded, highly filled polymer material based on PMMA.

We have therefore tried to provide a process which enables the preparation of highly filled, foamed polymer materials based on polymethylmethacrylate which  
30 maintains the characteristics necessary in cast resins, according to well tried technologies. We have now found a process which is suitable to achieve this object.

Accordingly, in one aspect, we provide a process for preparing highly filled, expanded polymer materials  
35 based on polymethylmethacrylate using carbon dioxide. In our process we use an initial solution VL, prepared from 70 to 95 parts by weight of methylmethacrylate and

5 to 30 parts by weight of polymethylmethacrylate prepolymer PP, from 0 to 5, optionally 0.05 to 5 parts by weight of a bifunctional cross linking agent and from 0 to 5, optionally, 0.5 to 1.5, preferably 0.5 to 5 parts by weight of a silanisation agent SI-M. A particle-like inorganic filler FS, in an amount of 30 to 80 wt.% (based on the expanded material as final product), is added to this initial solution VL with rapid agitation and carbon dioxide which is in the form of carbon dioxide snow or ice (crushed/ground) in an amount of 0.5 to 30 wt.% based on the resultant suspension, or in the form of gaseous carbonic acid, is uniformly distributed therein. While the polymerisation takes place, the solution is decarbonated by external heating or by the heat obtained in the polymerisation process, preferably by means of a Redox initiator system, and after the polymerisation, the removal from the mould can be carried out. The carbon dioxide may be added to the initial solution VL or to the resultant suspension.

Suitable prepolymers PP include, for example, conventional PMMA-polymers which contain, optionally, lesser amounts up to about 15 wt.% of suitable chosen comonomers such as methylacrylate. Normally, the prepolymers have a molar mass within the range of  $2 \times 10^4$  to  $4 \times 10^5$  Dalton [determined by size exclusion chromatography (SEC)]. It is also possible to add a cross-linking agent, for example in the form of a (meth)acrylic acid ester of multi-valent alcohols in amounts of 0.1 to 1.5 wt.% based on the monomers.

Suitable fillers FS are finely dispersed inorganic or organic materials normally used for cast resins. A grain size of a diameter of 200  $\mu\text{m}$ , preferably 60  $\mu\text{m}$  is, advantageously, not exceeded. If cristobalite is used as a filler, at least 95% of the particles should preferably be  $< 10 \mu\text{m}$ . Particles with a size of  $\leq 0.1 \mu\text{m}$  should not comprise more than 10 wt.% of the total

number of particles, if possible. The particle size is determined by conventional methods, (cf. B. Scarlett in "Filtration & Separation" pg. 215, 1965). In order to determine the particle size, the largest dimensions of the particles are used. Grain-like particles are preferred. Sometimes, it may be of advantage if the particles are freed from adsorbtively-bound moisture, e.g. by heating to about 150°C. The fillers FS may be natural or synthetically prepared products. The mechanical properties such as hardness and elastic modulus of shear can be determined according to the intended application of the cast resins. Here, an elastic modulus of shear of at least 5 GNm<sup>-2</sup> may be of advantage.

Suitable minerals include, for example, aluminium oxides, aluminium hydroxides and derivatives such as alkali and alkaline earth double oxides and alkaline earth hydroxides, clays, silicon dioxide in its various modifications, silicates, aluminosilicates, carbonates, phosphates, sulphates, sulphides, oxides, carbon, metals and metal alloys. Synthetic materials such as glass powder, ceramics, porcelain, clinker, and finely distributed synthetic SiO<sub>2</sub> are also suitable. Mention must be made of silicic acid modifications such as quartz (quartz powder), tridymite and cristobalite, as well as kaolin, talcum, mica, spar, apatite, baryte, gypsum, chalk, limestone, and dolomite. Mixtures of fillers may, optionally, also be used.

The amount of filler contained in the cast resins is preferably at least 40 wt.%. Generally an amount of 40 wt.% has not been exceeded. A filler content of the cast resins of > 50 and up to 80 wt.% is given as a guide. The fillers may be prepared in suitable grain sizes using conventional methods, for example crushing and grinding. Apart from aluminium hydroxide, cristobalite is particularly preferred.

In a preferred embodiment, the average particle

size is within the range of 60 - 0.5  $\mu\text{m}$ . Preferably, the hardness (according to Mohs: cf. Römpp's Chemie-Lexikon, 9th ed., p. 1700, Georg Thieme Verlag 1990) of the fillers FS is  $\geq 6$  in the case of cristobalite, and  
5 from about 2.5 - 3.5 in the case of aluminium hydroxide.

The silanisation agents SI-M are used, in a manner known per se, as adhesive agents between the filler and the organic phase. Prior art organosilicon compounds, may therefore, be used [D. Skudelny Kunststoffe 77, 1153  
10 - 1156 (1987); Kunststoffe 68 (1978); Firmenschrift Dynasilan®, Haftvermittler der Dynamit Nobel, Chemie]. These are primarily functional organosilicon compounds which have at least one ethylenically unsaturated group in the molecule. The functional group carrying the  
15 ethylenically unsaturated group is generally bonded to the central silicon atom by a C-atom. The remaining ligands on the silicon are normally alkoxy groups having 1 to 6 carbon atoms (ether bridges may also be contained in the alkyl group). Mention must be made of  
20 vinyltrialkoxysilanes. The C-C double bond may also be bonded to the Si-atom, via one or several carbon atoms, for example in the form of allyltrialkoxysilanes or  $\alpha$ -methacryloyloxypropyltrialkoxysilanes. Dialkoxysilanes may also be used, a further functional group with a C-C  
25 double bond, mostly of the same type, or an alkyl group preferably having 1 to 6 carbon atoms being bound to the Si-atom.

Different types of organosilicon compounds may also be present in the organosilicon component. These  
30 include, for example, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(methoxyethoxy)silane, divinylldimethoxysilane, vinylmethyldimethoxysilane, vinyltrichlorsilane,  $\alpha$ -methacryloyloxypropyltrimethoxysilane or  $\alpha$ -methacryloyloxypropyltris(methoxy-  
35 ethoxy) silane. The organosilicon compounds are preferably used together with catalysts of the amine type, more particularly of the alkyl amine type, having



3 to 6 carbon atoms, especially with n-butylamine. When using the amine catalyst, 0.05 to 10 wt.%, preferably 1 to 5 wt.%, of the organosilicon compound may be considered as a guide. Generally, the weight ratio  
5 between inorganic fillers and the organosilicon compound is 500 : 1 to 20 : 1, preferably 50 ± 25 : 1.

The process of the invention may be carried out according to known technical methods. Firstly the initial solution VL is prepared in a manner known per se.  
10 se. The initial solution advantageously contains the amine component and the silinisation agent Si-M. Then, the filler FS is introduced into the initial solution by means of a solubiliser, and then the resultant suspension is dispersed on the solubility. After the  
15 silanisation reaction, a part of the Redox component of the Redox initiator (Cf. H. Rauch-Puntigam, Th. Völker, Acryl- und Methacrylverbindungen, Springer-Verlag 1967) is advantageously added to the suspension and distributed by means of a blade agitator. Using  
20 conventional methods a polarisation inhibitor such as a sterically hindered phenol (Cf. Ullmanns Encyclopedia of Technology, 5th Ed. Vol. 20A, pg. 459-5-07, VCH 1992) and/or a lubricant such as a phthalic acid and/or lubricant such as a phthalic acid diester or stearic  
25 acid may also be added. Carbon dioxide is then added. Carbon dioxide may be added either as carbon dioxide snow, as ground CO<sub>2</sub>-ice or as a gas. A uniform distribution is of importance. When adding gas, the most suitable amount must be determined. A final  
30 addition of solid CO<sub>2</sub> to the amount of gas is not directly possible, since, when using solid CO<sub>2</sub>, a significant part is discharged from the suspension as a gas, into the air.

As soon as there is no further evidence of gas  
35 issuing from the suspension, the remaining Redox components of the suspension may be added, whilst stirring. During the resultant, exothermic Redox

polymerisation or, if peroxide initiators (See Rauch-Puntigam, loc.cit) are used exclusively, the suspension expands during hardening as a result of external heat.

Finally, the removal from the mould can take place.

- 5 The carbon dioxide may also be added to the initial solution VL, more particularly during the continuous preparation of the expanded polymer material. The suspension is prepared in suitable mixing aggregates. Suitable types are produced by Messrs.
- 10 Respecta/Düsseldorf/FRG or Coudenhove & Hübner/Vienna. The initiators may be added before the product leaves the mixer.

When using the method of the invention, an expanded PMMA with closed pores is normally obtained. Judging by  
15 the results so far, the density of the expanded plastics material is considerably lower, possibly by a half, compared with non-foamed PMMA despite the same amount of filler.

The process of the invention enables the  
20 preparation of a highly filled, expanded PMMA material in a relatively simple manner using conventional technology.

Because of the lower density of this material, many interesting applications are possible. The following  
25 Examples and drawings serve to illustrate the invention without limiting it in any way.

### Examples

#### A. Preparation of a highly filled suspension

30

##### Example A-1

60 g of a MMA-polymer ( $\eta$  spez/c = 130 - 140, Mw ca. 400,000, product PLEXIGUM® M 920 made by Röhm GmbH) is dissolved in 266.97 g of methylmethacrylate (MMA) and  
35 0.03 g of 2,4-dimethyl-6-tert.butylphenol at about 50°C over 5 hours, and then cooled to ambient temperature. 5.0 g of stearic acid and 3.0 g of glycoldimethacrylate

are dissolved in the resultant syrup. While gently stirring, 332.5 g of aluminium hydroxide with an average particle size of 45  $\mu\text{m}$  (product ALCOA ® C33 made by ALCOA/USA) and then 332.5 g of aluminium hydroxide with an average particle size of 8  $\mu\text{m}$  (product ALCOA ® C333) are introduced into the syrup on the solubiliser or dissolver. (product Dispermat ® of Messrs VMA Getzmann/FRG). Thereafter, the suspension is dispersed with the solubiliser with 12.5 m/s for about 10 minutes.

10

#### B. Preparing the expanded polymer material

##### Example B-1

700 g of the highly filled suspension, prepared according to Example A-1 are measured into a polyethylene beaker ( $\phi = 9$  cm,  $H = 15$  cm). Whilst stirring by means of a blade agitator, 7 g of dibenzoylperoxide, 50% in di-butyl phthalate (product INTEROX ® BP-50-FT made by Peroxide Chemie GmbH) and 3.5 g azo-bis-iso-butyronitrile (product INTEROX ® NN IBN) are added at about 25°C and dissolved. Whilst stirring, 7.0 g of CO<sub>2</sub> snow are then added to the suspension. After stirring for 5 minutes, the temperature of the suspension is measured. Thereafter, whilst stirring, 7.0 g of N,N-dimethyl-p-toluidine is added as a 50% solution in MMA to the suspension. After stirring for 1 minute, the stirrer is removed. A polymer foam is obtained which is characterised in Table 1.

##### 30 Example B-2

Using a method analogous to that of B-1, instead of 7.0 g of CO<sub>2</sub>-snow, 35.0 g of CO<sub>2</sub>-snow is added to the suspension.

##### Example B-3

35 Using a method analogous to that of B-1, instead of 7.0 g of CO<sub>2</sub>-snow, 70.0 g of CO<sub>2</sub>-snow is added to the suspension.

Example B-4

Using a method analogous that of B-1, instead of 7.0 g of CO<sub>2</sub>-snow, 140.0 g of CO<sub>2</sub>-snow is added to the suspension.

5

TABLE 1

Data to Examples B-1 to B-4

10	Example	Addition CO <sub>2</sub> -snow (%)	Temp.after stirring for 5 mins. (degree C)	Hardening time (min)	Density of the foam (g/cm <sup>3</sup> )
	B-1	1.0	+ 20	12	1.12
	B-2	5.0	+ 10	15	0.84
	B-3	10.0	- 5	20	0.66
	B-4	20.0	- 15	Foam collapses before hardening	

15

Characteristics of the expanded polymer materials:

According to the process of the invention, foams are obtained which have largely closed pores. Figures 1-3 show in cross-section foamed products of the invention.

20

As shown by the Figures 1-3 (Figure 1: with 5 wt.% of CO<sub>2</sub>-snow; Figure 2: with 5 wt.% of CO<sub>2</sub>-ice, ground; Figure 3; with 10 wt.% of CO<sub>2</sub>-snow), the average pore size increases as the CO<sub>2</sub> amount increases. The correlation between the foam density and the CO<sub>2</sub> addition is apparent from the graph in Figure 4.

25

Claims

1. A process for preparing a filled, expanded polymer material based on polymethylmethacrylate in which a  
5 particle-like inorganic filler FS, is introduced with agitation and in an amount of 30 to 80 wt.% based on the resultant suspension into a solution VL prepared from 5 to 70 parts per weight of methylmethacrylate and 1 to 15 parts by weight of polymethylmethacrylate prepolymer PP,  
10 thereby forming a suspension, and gaseous or solid carbon dioxide in fine distribution is uniformly introduced into the initial solution or suspension, whereby in consequence either of external heating or the heat effect of the polymerisation process when  
15 initiated, carbon dioxide is expelled while the polymerisation takes place.

2. A process as claimed in claim 1, in which the carbon dioxide is introduced as carbon dioxide snow or  
20 as ground carbon dioxide ice in an amount of 0.5 to 30 wt.%, based on the suspension formed.

3. A process as claimed in claim 1 or 2, in which aluminium hydroxide is used as a filler.  
25

4. A process as claimed in claim 1 or claim 2, in which cristobalite is used as a filler.

5. A process as claimed in any of claims 1 to 4  
30 wherein the solution VL additionally includes from 0 to 5 parts by weight of a bifunctional cross-linking agent and from 0 to 5 parts by weight of a silanisation agent.

6. A process as claimed in any of claims 1 to 5  
35 wherein the filler has a grain size of 50  $\mu\text{m}$  or less.

7. A process as claimed in any of claims 1 to 6

wherein the amount of filler in the polymerised resin is from 50 to 80% by weight.

8. A process as claimed in claim 1 substantially as  
5 hereinbefore described and with reference to the accompanying Examples.

9. A process as claimed in claim 1 substantially as  
hereinbefore described and with reference to the  
10 accompanying drawings.

**Relevant Technical Fields**

- (i) UK Cl (Ed.M) C3C  
(ii) Int Cl (Ed.5) C08J

Search Examiner  
M J PRICE

Date of completion of Search  
27 JULY 1994

**Databases** (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant  
following a search in respect of  
Claims :-  
1-9

(ii) ONLINE DATABASES: WPI

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